

## **METHOD FOR THE AUTOMATED MANUFACTURE OF PURE SO<sub>2</sub> FROM SULFUR AND OXYGEN**

Obtaining SO<sub>2</sub> from elemental sulfur is a process widely used in the industry. Nevertheless, when a high purity product in industrial amounts and furthermore not polluting the environment is required; the processes fulfilling these requirements are either for small productions, they inevitably produce pollution or they require many purification unit operations, due to the use of air or hydrocarbons as comburent agent or sulfur to oxidize as a liquid.

The process described in present invention corresponds to an oxidation overcoming the aforementioned general limitations and further carrying out a control of the energy and the purification unit operations better than those standard known ones.

US Patent 5,204,082 by Schendek (1993) describes a method for preparing high purity SO<sub>2</sub> based on the submerged combustion of elemental sulfur in liquid state, using both air and pure oxygen. This method has the inconvenient of trailing particles of unburned sulfur from the liquid sulfur present both as a reagent and as a solvent. Thus the method uses different unit operations for removing these particles of sulfur trailed from the combustion phase.

This combustion has the characteristic of having excess of sulfur relative to the reaction air or oxygen, producing a combustion generating side reactions of the sulfur giving reaction by-products; the main purpose of the method is to remove the sulfur from the combustion gases for purifying the SO<sub>2</sub> without considering the gases other than SO<sub>2</sub>.

Therefor it is necessary to carefully control the melted sulfur temperature because the variation of its viscosity with the temperature, in order to avoid the difficulties in the liquid sulfur flow being burnt. In other words, this submerged combustion has the characteristic of requiring a good control of liquid sulfur temperature and its subsequent recycling for obtaining high purity without major concern of gaseous by-products produced together with SO<sub>2</sub>.

US Patent 6,045,770 by Battles (2000) describes the preparation of SO<sub>2</sub> from granulated or emulsified sulfur, by oxidation with air in a sulfur combustion furnace. The reaction from a sulfur emulsion consisting in a suspension of sulfur (70%) in water (30%) with sulfur particles of 4-6 μm is carried out in a sulfur burner atomizing it to sulfur frog or mist for its combustion in a sulfur furnace. The moisture during the combustion generates sulfuric acid as a significant polluting agent from the process.

As sulfur powder can explode, the combustion with granulated sulfur requires an inert gas such as nitrogen or CO<sub>2</sub> serving as inert medium or diluent agent of the combustion reagents, thus avoiding an eventual lack of control not only of the temperature but also of the combustion products types.

The processes of submerged combustion and of combustion of atomized sulfur with air, described above, have the characteristic of requiring a safe control of the liquid sulfur temperature due to its abrupt viscosity variations with the temperature; furthermore, the sulfur sublimates and forms crystals when condensing, so as the sulfur storage tanks require to be properly protected against these temperature changes.

The industrial solid sulfur normally is also accompanied by traces of hydrogen sulfide, H<sub>2</sub>S, or of hydrocarbons being constituents of the sulfur source and emitted to the atmosphere transformed after the combustion.

JP Patent 26011 by Chibooru B. (Bayer AG, 1983) uses the sulfur combustion with oxygen at 1000-1100°C adding sulfuric acid of 20 to 90% concentration, instead of 800 – 1300°C required without adding sulfuric acid. Nevertheless, the purity of the SO<sub>2</sub> produced is not high, specially when for this low temperature it is required further addition of hydrocarbons as fuel compensating the lower temperature.

JP Patent 309707 by Araki K. (Mitsubishi Heavy Ind. Ltd., 1997) describes an equipment to produce high purity SO<sub>2</sub>, based on the combustion of solid sulfur with oxygen or with oxygen enriched air. The combustion gases are cooled with H<sub>2</sub>O; the SO<sub>3</sub> is removed with a humid type electric powder collector and a gas separator for removing the unreacted O<sub>2</sub>, CO<sub>2</sub> and N<sub>2</sub>, in its case. Nevertheless, this system requires various purification steps to obtain a high purity SO<sub>2</sub>.

These patents allow to appreciate that all the described processes require working with the impurities produced in the sulfur oxidation, or combustion, in order to arrive to a process offering pure SO<sub>2</sub>.

Present invention permits to avoid not only the critic control of the oxidation temperature itself, but to simplify the unit operations as the combustion with pure oxygen, diluted with SO<sub>2</sub> produced in the system itself as a closed system, makes its advantages clear for any skill in the art, the thermically autocontrolled oxidation producing high purity SO<sub>2</sub>. The automation introduced in this invention allows not only a better control of the process, but also a production of variable capacity.

### Description of the drawings

Figure 1 is a flowsheet representation showing the system of production of SO<sub>2</sub> from the sulfur feed to the final SO<sub>2</sub> exit and the back of the latter as diluent and cooling agent of the oxidation reaction, with liquefaction by a cooling plant.

Figure 2 represents the electronic circuit of the plant automated control showing the oxygen sensors and the flow sensors and their respective control connections.

Figure 3 is a schematic diagram of the burner showing the admissions and the distribution of the comburent gas, as primary, secondary and tertiary gas used for the controlled combustion of the atomized sulfur.

Figure 4 shows the production plant of SO<sub>2</sub> with the system of liquefaction by compression (15).

### DESCRIPTION OF THE INVENTION

The SO<sub>2</sub> automated production system described in present invention corresponds to the plant automated control based on oxygen sensors and on oxygen and sulfur flow sensors. Furthermore, this description shows how by varying the amounts of liquid SO<sub>2</sub> or final product, the flows of oxygen, sulfur and unliquefied return SO<sub>2</sub> vary under control.

Accordingly, a description of the process carried out for an amount of 5 to 30 tons per day will be provided taking into account that for amounts above 30 tons per day a burner having larger capacity is required.

The description of the process is made with reference to the general flowsheet shown on figure 1. The incorporation of sensors for oxygen, for the sulfur flow and for the SO<sub>2</sub> flow is shown on figure 2 specifically representing these components of the process. The features of the combustion are made by reference to figure 3 representing the structure of the burner with its atomizer for a production capacity not higher than 30 tons per day. For higher productions only the change of the burner and a combustion chamber suitable for said capacity are required. On the other hand, figure 4 represents the liquefaction system of the SO<sub>2</sub> produced by compression as an alternative to the system of liquefaction only by cooling.

Figure 2 represents in detail the control diagram of the automated process. In this figure it is shown: the return oxygen sensor, AE/AIT-17, entering together with the return SO<sub>2</sub>, measured with the flow sensor FIT 17; the pure oxygen flow sensor, FIT 09; the sulfur flow sensor, FIT 05, as well as the respective control connection.

Thus, according to the details of figures 1 to 4, a 170 kg/h flow of sulfur in solid or liquid state is entered into the storage tank (1) and then maintained at a temperature of 125 - 130°C with the steam produced following the combustion chamber (4) in the heat exchanger (10) of this process. This sulfur enters into the feed tank (2) maintained at a temperature from 130 to 135°C with the same steam produced after the combustion of the sulfur in the multistep exchanger (10); this steam is the same that, after transferring part of its heat to the feed tank (2) is carried to the storage tank (1). These two steps have the purpose of maintaining the sulfur in liquid state for its handling and for removing the impurities proper of the delivery, in particular the most heavy ones, and the moisture.

The feed sulfur is maintained liquid in the range of 130 – 135°C in the feed tank (2) and therefrom is fed to the atomizer (3), represented in detail in figure 3, with a standard fluid pump (5), as at this temperature it offers no problem of viscosity. In this temperature range, the viscosity is lower than 10 mPa/s. As an antecedent, the sulfur under 160°C rapidly increases its viscosity to reach values of 80,000 mPa/s at 190°C. The liquid sulfur is introduced in the burner (3) being part of the combustion chamber (4).

Figure 3 shows in detail the structure of the burner (3). The SO<sub>2</sub> return (17) containing oxygen non consumed from previous oxidation is enter into this burner; pure oxygen (9) is added to this SO<sub>2</sub> before entering into the burner thus forming the fuel with SO<sub>2</sub> as diluent and cooling agent.

The liquid sulfur is entered (5) through the central back part of the burner (3) and through another also back entrance (6), parallel to the sulfur entrance (5), the O<sub>2</sub> enriched return SO<sub>2</sub> called "primary gas" (6) is entered. The primary gas is the one introduced in wrapping form with the liquid sulfur which is then pulverized by effect of the high speed of the mobile cup of the atomizer in the burner producing microdrops. This mixture of SO<sub>2</sub>, oxygen and finely pulverized sulfur in microdrops leaves the rotatory cup of the atomizer and enter into the combustion chamber (4) where the sulfur oxidative combustion step occurs transforming the sulfur in pure SO<sub>2</sub> by the action of oxygen being part of the combustion gas and called tertiary gas (8).

The rest of the return flow internally wraps the burner acting as cooler and thermally isolating all the front of the burner, and it is called secondary gas (7); in said function, the gas is thus pre-heated in the inner of the combustion chamber (4) wherein it dilutes and cools the total mass produced in the combustion. This is the tertiary gas (8).

therewith the temperature does not exceed 1231°C in the combustion chamber due to the diluting and cooling effect of the SO<sub>2</sub>.

This temperature control in the combustion chamber inner (4) is reached by a suitable handling of the SO<sub>2</sub> return gases (17) by means of the automation based on the return oxygen; therewith a temperature above 1144°C ± 50°C and lower to 1231°C is reached. In said conditions, the process is easily controlled resulting in a high purity SO<sub>2</sub>.

The combustion gases at the temperature of 1167 ± 50°C are following passed through a heat multistep exchanger with water (10) shown in figure 1, and steam is produced at a temperature range of 145 – 160°C mainly used for maintaining in liquid state the feed sulfur (2) entering into the burner (3) and the storage one (1). The steam excess produced can be used for other heat exchange unit operations in an industrial chemical plant.

The effluent of the sulfur to SO<sub>2</sub> conversion, leaving the multistep heat exchanger at a temperature above or equal to 192°C, is treated in a heat exchanger with atmospheric air (11), so as when leaving it, the combustion gas temperature is 85±5°C.

The gases pass then into a tower (12) removing SO<sub>3</sub> and the moisture that eventually could enter into the system, with concentrated 98% H<sub>2</sub>SO<sub>4</sub> (13) at 30°C. This tower is provided with a sulfuric acid drop trap (14) so as the gases passing therein essentially comprise SO<sub>2</sub> and O<sub>2</sub> unreacted in the combustion chamber.

The whole mass of gases from the combustion chamber is moved by means of a blower (18) and the mass entering into the cooling plant is moved with the blower (19); the mass returning to the combustion chamber is moved with the blower (20).

From the total mass moved by the blower (18) up to a 30% is circulated to the cooling plant (15) by means of the blower (19). This cooling plant works at a temperature from -30 to -60°C. From this gas fraction, a high part is liquefied and comprises the SO<sub>2</sub> as final product (16) and the other cooled part comprises essentially SO<sub>2</sub> and O<sub>2</sub>; both gases re-enter into the system through the blower (20). This return SO<sub>2</sub> (17) comprising about the 80% of the total SO<sub>2</sub> flow is driven to the combustion chamber (4) but, before entering thereinto it is mixed with the pure oxygen (9) in order to form the comburent mixture entering into the combustion burner.

Thus the produced SO<sub>2</sub> participates in a closed system or circuit for acting then as diluent and cooling agent of the elemental sulfur oxidation.

As an alternative to the aforementioned process of SO<sub>2</sub> liquefaction by cooling, the also efficient way of liquefaction by means of a compressor working between 3,8 and 5,0 bar of pressure together with cooling by water allowing an easy controlled liquefaction can be used. This is shown in figure 4 wherein it can be appreciated an automated SO<sub>2</sub> production plant producing liquid SO<sub>2</sub> by compression with its compression unit (15) and the lung tank (21). The non compressed gases return to the recycling system through the lung tank, therefrom a blower (20) integrates it to the rest of the SO<sub>2</sub> returning to the combustion chamber (4).

It must be pointed out that the above described method always works in the absence of nitrogen (the oxidant agent is pure oxygen) different to other industrial

systems for the production of SO<sub>2</sub>. The storage tank (1) wherein the sulfur is maintained liquefied between 125 – 130°C, is provided with a funnel with chimney and forced air extraction permitting to evacuate the moisture and the nitrogen present in the sulfur, thus all non desired possible nitrogen impurity is removed in the closed circuit system that the plant has at the moment of burning the sulfur.

The start point of the process in the plant is initiated with a scavenging with pure oxygen of the whole closed circuit for removing all traces of nitrogen and other gases accompanying the air which eventually could contaminate the liquefied SO<sub>2</sub> production. This sweep with oxygen is thrown to the atmosphere through the cooling plant or the compression plant if that alternative of liquefaction is used, before initiating the combustion process and the SO<sub>2</sub> liquefaction. Thus, the SO<sub>2</sub> production method is free of the presence of nitrogen or other gas different from pure oxygen.

The chemical analysis of sulfur allows to include as a significant impurity thereof, aromatic polycyclic hydrocarbons, detected by extracting with acetonitrile and by UV an HPLC as standard analysis technique. Analyses of SO<sub>2</sub> produced at the exit of the cooling plant are also carried out, the maximum impurity of SO<sub>2</sub> corresponding to traces of sulfonated polycyclic hydrocarbons; the sulfonation occurs after the sulfur in oxidation passes by the combustion chamber. The analyses show that the impurity does not exceed 0.05%, without discarding the eventual presence of moisture and H<sub>2</sub>SO<sub>4</sub> in parts per million.

As can be appreciated, the control logic is based on the regulation of the O<sub>2</sub> flow at the entrance of the burner based on the S flow and the SO<sub>2</sub> being the cooling and diluent agent of the reaction. The control is carried out by modifying the amount of O<sub>2</sub> so

as to have a constant O<sub>2</sub>:S ratio in function of the returned O<sub>2</sub> together with the SO<sub>2</sub> with a light excess not exceeding the 5% of the stoichiometric one.

The flows involved in the control, represented on figure 2, are:

F05: S flow

F09: O<sub>2</sub> flow

F17: cooling/diluent flow.

For measuring the S flow, F 05, a sonic type flow sensor (FE/FIT-05) is used. The O<sub>2</sub> flow, F09, is measured in the same manner and the flow of the returned SO<sub>2</sub> F17 is measured with FIT-09) and FIT-17) rotameters, respectively. The sulfur flow is adjusted by the proportional valve FV.05 and the O<sub>2</sub> is controlled with a proportional valve FV-07. The content or concentration of O<sub>2</sub> in the F17 flow is measured by a O<sub>2</sub> sensor (AE/AIT-17).

The first control connection consists in the regulation of the S flow to the burner by the flow meter 05 and the control valve 05.

The second connection control consists in the regulation of the O<sub>2</sub> flow by the flow meter 09 and the control valve 09. The adjustment of the flow is carried out such as to maintain constant the S:O<sub>2(total)</sub> ratio. The total O<sub>2</sub> is obtained from the addition of pure O<sub>2</sub> plus the return O<sub>2</sub>, the latter being calculated by the flow sensor 17 and the O<sub>2</sub> analyzer 17.

The control system allows the adjustment of the oxygen up to a maximum of 5% excess on the stoichiometric one.

The sulfur oxidation reaction or combustion is previously evaluated in order to know the amounts and proportions of the reactants to be mixed for their reaction; this is

carried out with the HSC reaction simulated program of Outokumpu<sup>(TM)</sup>. This program provides the reaction temperature reached in the combustion chamber for different O<sub>2</sub>, S and SO<sub>2</sub> mass ratios of the oxidation closed circuit in different mixtures.

For example, for:



if the reactants and return SO<sub>2</sub> masses are that following indicated, the predicted reaction temperature is the included in the fourth column of the following Table.

S (g)	O <sub>2</sub> (g)	SO <sub>2</sub> (g)	T (°C)
32.00	32.64	0	5018.8
32.00	33.60	0	5018.7
32.00	32.63	243.42	1211.56
32.00	33.60	243.42	1211.53
32.00	32.63	256.23	1167.57
32.00	33.60	256.23	1167.55
32.00	32.63	262.64	1146.88
32.00	33.60	262.64	1146.75

The temperature reached in the combustion chamber mainly depends on the S:O<sub>2</sub>:SO<sub>2</sub> ratio and not so much on the temperature of the fuel entering into the burner; if the temperature of the SO<sub>2</sub> entering into the burner is variable, the reaction temperature is the one indicated for the ratio, expressed in grams, as follows:

$$S : O_2 : SO_2 = 32 : 33,6 : 256,2$$

<u>Temperature of the return SO<sub>2</sub></u>	<u>Reaction temperature</u>
0°C	1164,77°C
15°C	1167,55°C
30°C	1175,93°C
50°C	1187,28°C

The above description with the features of the oxidation process itself without gases generating byproducts, such as nitrogen, and only with pure oxygen diluted with SO<sub>2</sub> produced in the closed circuit system; the SO<sub>2</sub> high purity controlled by analysis before and after the combustion; its stepping for different production capacities; the different routes for obtaining liquid SO<sub>2</sub> either by cooling or compression; as well as the oxidation process computer simulation indicate for any skill in this area of processes that the system offers significant advantages relating to the state of the technique not automated and not working under closed circuit such as the one described in present patent application.

The automated control of the flows of sulfur and oxygen carried out based on the return oxygen, is the base of the efficiency of the process for obtaining high purity liquefied SO<sub>2</sub> in safe manner free of any environmental contamination.